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# A NEW MODEL FOR HYDROGEN ABSORPTION IN WELDS

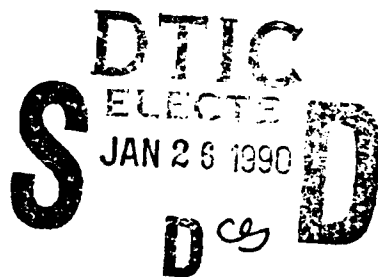
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ABSTRACT

↙ A systematic review of previous research has shown that the use of Sievert's law to calculate the hydrogen absorption reaction temperature in the weld pool is invalid. A new model of hydrogen absorption is proposed which can explain both previously measured data and the data obtained in this study.

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## INTRODUCTION

The most often used equation to describe the absorption of hydrogen in steel is the well known Sievert relationship which is based on the equilibrium reaction



Using the tabulated free energy of this reaction,<sup>1</sup> the equilibrium constant as a function of temperature is

$$K = \text{H} / (\text{P}_{\text{H}_2})^{1/2} = \exp (-4388 / T + 5.55). \quad (2)$$

This equation can be used to plot the absorbed hydrogen,  $\text{H}$ , as a function of the diatomic hydrogen partial pressure,  $\text{P}_{\text{H}_2}$ , for various assumed equilibrium reaction temperatures as shown in Figure 1. This data has been replotted in Figure 2 as the amount of absorbed hydrogen as a function of the assumed reaction temperature for various hydrogen partial pressures. As can be seen, the amount of absorbed hydrogen increases with both temperature and hydrogen partial pressure. Through the use of free energy interaction coefficients, it has been shown<sup>2</sup> that these values are valid to within 5% for both iron and steel alloys.

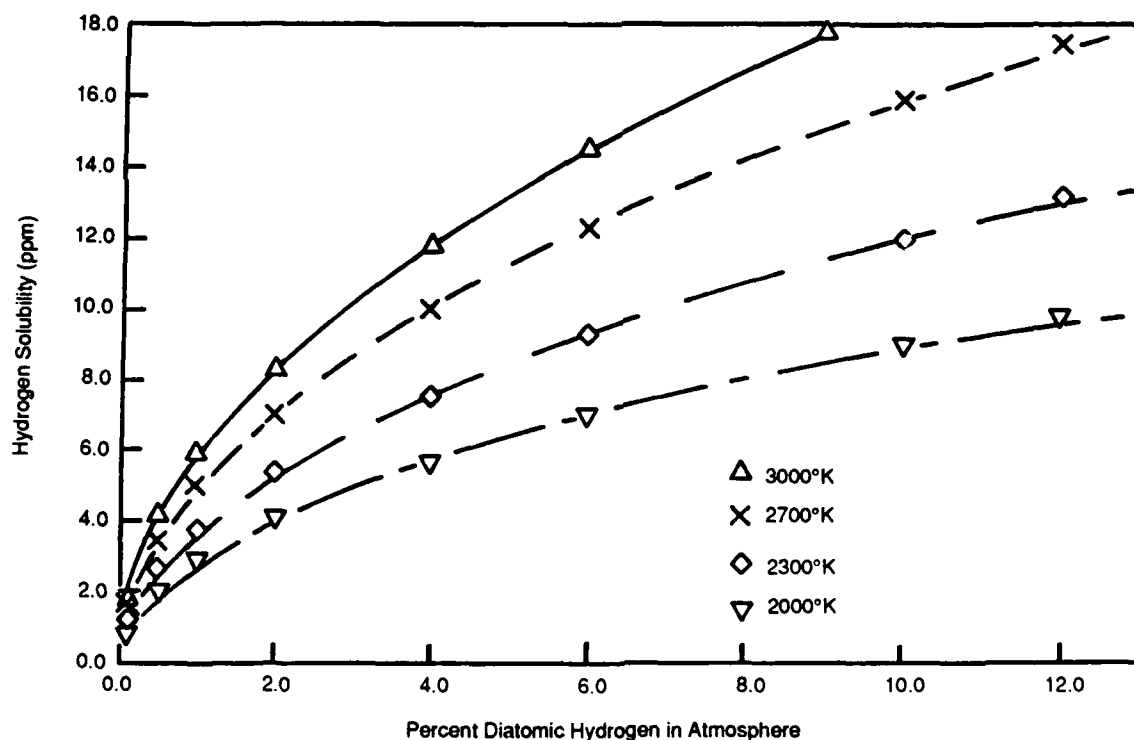


Figure 1. Equilibrium hydrogen solubility as a function of diatomic hydrogen partial pressure for various assumed absorption temperatures.

1. ELLIOT, J. F., GLEISER, M., and RAMAKRISHNA, V. *Thermochemistry for Steelmaking, Vol. II*. Addison-Wesley Publishing Co., Reading, MA, 1963.
2. GEDEON, S. A. *Hydrogen Assisted Cracking of High Strength Steel Welds*. U.S. Army Materials Technology Laboratory, MTL TR 88-12, May 1988.

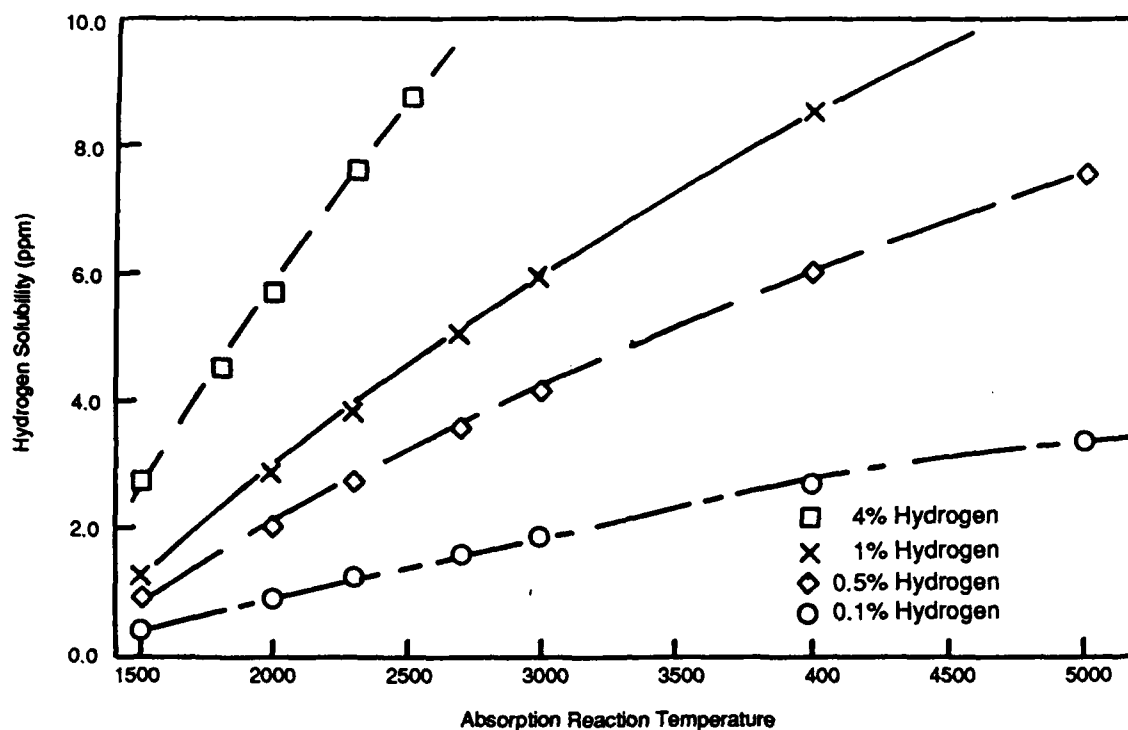


Figure 2. Equilibrium hydrogen solubility as a function of the absorption temperature for various diatomic hydrogen partial pressures.

Many previous investigators have used the results of diffusible hydrogen measurements (rather than  $H$ ) in their hydrogen absorption reaction temperature calculations. This can lead to significant errors since the value of hydrogen measured in this test does not equal the amount of hydrogen initially absorbed by the weld pool. Diffusible hydrogen measurements can be converted to initially absorbed hydrogen values by using Terasaki's theoretical analysis.<sup>3</sup> Terasaki has recognized that a significant amount of the total hydrogen will be lost through diffusion of hydrogen out of the sides of the specimen within seconds after solidification of the weld pool. To illustrate this, he has calculated the ratio of hydrogen remaining in the sample to the initial hydrogen as a function of the thermal factor for various specimen and weld bead sizes (Figure 3). His thermal factor is the integral of the diffusion constant over time. The thermal factor associated with a water-quenched TWI diffusible hydrogen specimen<sup>4</sup> is indicated in Figure 3.

Terasaki's analysis shows that even a 2.5-cm-thick (1 in.) specimen will lose a substantial amount of hydrogen during the time it takes to quench the diffusible hydrogen specimen. Using Terasaki's analysis and knowing the specimen size, weld size, and the time to quench, the amount of hydrogen initially absorbed into the weld pool can be estimated from the amount of hydrogen measured in the diffusible hydrogen test. It should be noted that Terasaki does not consider the amount of hydrogen which will be lost through the top surface of the weld. Thus, his values are quite conservative, and the actual ratio will be even less than his analysis shows.

3. TERASAKI, T., AKIYAMA, T., HAMASHIMA, S., and KISHIKAWA, K. *An Analysis on Specimen Size for Determination of Diffusible Hydrogen Content in Weld Metal*. Trans. Japan Welding Society, v. 17, no. 1, 1986, p. 93-101.

4. *The Measurement of Diffusible Hydrogen in Manual Metal Arc Weld Metal Deposits*. IIW II-576-82, 1982.

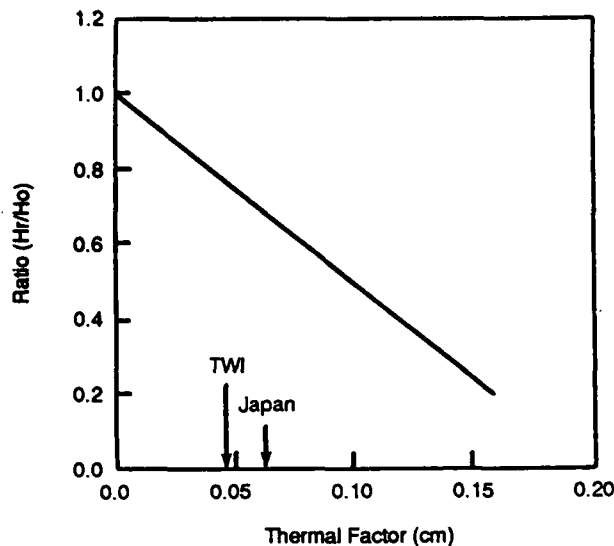


Figure 3. Ratio of retained hydrogen to initially absorbed hydrogen as a function of the "thermal factor" (after Terasaki, Ref. 3). This figure assumes SMPW, a 0.22-cm bead depth, a 2.5-cm specimen thickness, no weld-bead reinforcement, and no diffusion through the top surface of the weld specimen.

Comparing the hydrogen absorption data of previous investigators (as corrected by Terasaki's analysis) with Figure 1 (using Sievert's law in Equation 2), the reaction temperatures found for the absorption of hydrogen in gas metal arc welds (GMAW) is in excess of 3000°C, which is the approximate boiling temperature of iron. This value is unreasonably high. Block-Bolten and Eagar<sup>5</sup> have shown that evaporative cooling of iron vapors will limit the maximum temperature of a weld made on steel to 2500°C. Howden and Milner<sup>6</sup> have shown that iron vaporization will also limit the amount of hydrogen which can come into contact with the weld pool at high temperatures. Spectroscopic research by Quigley et al.,<sup>7</sup> has shown that vaporization will significantly reduce the arc power transferred to the workpiece; they showed the weld pool temperature to be between 2400K and 2750K (a maximum of under 2500°C). Other research by Quigley,<sup>8</sup> found that evaporation is the dominant mechanism for energy loss from the weld pool. Krause,<sup>9</sup> using an optical spectral radiometric/laser reflectance method, determined the maximum surface temperature of a gas tungsten arc (GTA) weld to be approximately 2800K.

Salter,<sup>10</sup> collecting data by arc melting metal on a water-cooled copper hearth, found that the arc significantly aided hydrogen transfer to the pool. Based on Sievert's law, he postulated that hydrogen was absorbed into the central "hot spot" of the pool at a temperature well in excess of 2500°C; a temperature now known to be impossible to achieve. He also found that increasing the hydrogen content of the gas increased the calculated temperature of the weld pool.

5. BLOCK-BOLTEN, A., and EAGAR, T. W. *Metal Vaporization from Weld Pools*. Met. Trans., v. 15B, no. 3, 1984, p. 461-469.
6. HOWDEN, D. G., and MILNER, D. R. *Hydrogen Absorption in Arc Melting*. British Welding Journal, June 1963, p. 304-316.
7. QUIGLEY, M. B. C., RICHARDS, P. H., SWIFT-HOOK, D. T., and GICK, A. E. F. *Heat Flow to the Workpiece from a TIG Welding Arc*. J. Phys. D: Appl. Phys., v. 6, 1973, p. 2250-2258.
8. QUIGLEY, M. B. C. *Physics of the Welding Arc*. Welding and Metal Fabrication, December 1977, p. 619-626.
9. KRAUSE, H. G. *Experimental Measurement of Thin Plate 304 SS GTA Weld Pool Surface Temperatures*. Welding Journal, v. 66, no. 12, 1987, p. 353a-359a.
10. SALTER, G. R., and MILNER, D. R. *Gas Absorption from Arc Atmospheres*. British Welding Journal, February 1960, p. 89-100.



White,<sup>11</sup> studying hydrogen in GMAW, did not establish an equilibrium reaction temperature, but rather concluded that increasing hydrogen contents increased the temperature of the weld pool. Using her data for diffusible hydrogen content of GMA welds as a function of hydrogen added to the weld shielding gas, Sievert's law predicts temperatures in excess of 2500°C.

Savage et al.,<sup>12</sup> found that water vapor added more hydrogen to the weld than did an equal amount of hydrogen gas. They also found that a pulsed arc was more stable in the presence of hydrogen than welding with direct current reverse polarity (DCRP). They did not attempt to explain these occurrences, but if their data is reinterpreted to account for hydrogen diffusing away from the weld for 10 seconds, then Sievert's law predicts a reaction temperature in excess of 2500°C.

Howden and Milner<sup>6</sup> used a stationary arc in an enclosed chamber to study both the hydrogen absorbed in the molten pool and the hydrogen retained in the solidified metal. They found that thoroughly deoxidized iron will absorb much less hydrogen than iron which contains a normal amount of oxygen. Using Sievert's law, the reaction temperature associated with the hydrogen absorption in iron-containing oxygen is well in excess of 2500°C.

Chew and Willgoss,<sup>13</sup> studying GTAW, realized that they were not analyzing the initially absorbed hydrogen and, instead, measured what they termed an "effective reaction temperature" rather than an absorption reaction temperature. Thus, their results were strongly dependent on the heat input and cooling rate. They found that an increase in current decreases the amount of hydrogen and decreases the effective reaction temperature (even though increasing the current should increase the weld pool temperature and, thus, increase the absorption temperature). Thus, Chew and Willgoss' effective reaction temperature does not measure the absorption temperature, but rather reflects a decrease in the cooling rate, which allows more hydrogen to escape. If their diffusible hydrogen results are converted to initially absorbed hydrogen, the calculated hydrogen absorption reaction temperature using Sievert's law is in excess of 2500°C (since they followed the IIW procedure, a time to quench of 5 seconds is assumed in this conversion).

Research performed on the solubility of nitrogen in arc-melted iron<sup>14</sup> concluded that nitrogen absorption obeyed Sievert's law, but that the arc resulted in a substantial increase in solubility. This conclusion was based on the fact that the experimental curve was parabolic, and the deviation from the normal Sievert law prediction was attributed to "energy acquired by nitrogen molecules in the anode boundary zone through interaction between electrons and neutral particles." However, the dissociation energy for hydrogen is far less than for nitrogen, so the effect of an arc increasing the solubility in excess of that predicted by Sievert's law would be greater for hydrogen than for nitrogen.

Thus, by analyzing the data of previous researchers on hydrogen absorption, it has been shown that Sievert's law cannot be directly used to assess the hydrogen absorption reaction temperature. Previous research using Sievert's law has been shown not to accurately reflect a true hydrogen absorption temperature which must not exceed the maximum surface

11. WHITE, D. R. *In Process Measurement of Hydrogen in Welding*. Ph.D. dissertation, University of Illinois, Champaign, IL, 1986.

12. SAVAGE, W. F., NIPPES, E. F., and HUSA, E. I. *Hydrogen-Assisted Cracking in HY-130 Weldments*. Final Report to the Office of Naval Research, Contract No. N00014-75-C-0944, NR 031-780, January 1981.

13. CHEW, B., and WILLGOSS, R. A. *Weld Metal Hydrogen Absorption During TIG-Welding with Argon-Hydrogen Gas Shields*. Proc. Weld Pool Chemistry and Metallurgy International Conference, London, April 1980, p. 155-165.

14. *The Anode Boundary Region in Argon Shielded Tungsten Arcs*. IIW Doc. 212-640-86, 1986.

temperature of the weld pool. The assumption of a one-step absorption process which neglects the effects of dissociation, solute rejection upon solidification, and diffusion of hydrogen away from the weld region, is too simplistic to provide realistic values of the absorption temperature.

The major assumption in the Sievert relationship, equilibrium absorption of diatomic gas by the weld pool, must be reconsidered. This study examines the postulate that hydrogen absorption can be modelled by assuming a two-step absorption process. It is postulated that diatomic hydrogen will dissociate in the high temperature regions of the welding arc, and both diatomic and monatomic hydrogen will absorb into the weld pool at the temperature of the weld pool surface. In order to understand this, a number of aspects of the problem will be discussed: (1) monatomic hydrogen absorption, (2) dissociation, (3) the temperature at which dissociation takes place, (4) the effect of temperature distribution on the weld pool surface, and (5) the effect of solute rejection of hydrogen upon solidification.

### EXPERIMENTAL PROCEDURE

In order to verify the evaluation of previous research and accurately determine the amount of hydrogen initially absorbed into the molten weld pool, diffusible hydrogen measurements were performed in our laboratories. Hydrogen measurement technique variations were investigated to determine the effect on the accuracy and reproducibility of the final numerical result. Technique variations which were studied included: specimen size, specimen material, specimen surface finish, outgassing temperature, outgassing time, calibration procedure of the gas chromatograph, and time delay between weld completion and quench.

The results of this study have been reported by Gedeon,<sup>2</sup> and a number of these variations have also been studied by the recent AWS A4.3-86 committee.<sup>15</sup> However, a number of the pertinent procedures and results are noted herein.

The hydrogen was measured with a Yanaco hydrogen analyzer, model G-1006. This unit uses a thermistor-type thermal conductivity detector, argon carrier gas, and molecular sieve 5A in the column. A gas chromatography method was used because solubility errors associated with outgassing under glycerin are eliminated because one can ensure that only hydrogen is being measured rather than all gasses being collected, and because a leaking outgassing chamber can be detected due to the ability to measure nitrogen, as well as hydrogen.

The AWS A4.3-86 specimen size was utilized because it is the maximum width and depth that will fit into the Yanaco outgassing chambers. The AWS A4.3-86 length was used in order to be able to compare data from one lab to another.

A 45°C outgassing temperature was chosen. Previous work has shown that hydrogen will become trapped at various defects and imperfections in the crystal lattice. This trapped hydrogen will be activated and allowed to outgas at temperatures in excess of 100°C.<sup>16</sup> Thus, higher outgassing temperatures will result in more measured hydrogen because a portion of the residual hydrogen will be measured, as well as the diffusible hydrogen. Nonetheless, the 45°C outgassing temperature was found to give consistent results.

15. *Standard Procedures for Determination of the Diffusible Hydrogen Content of Martensitic, Bainitic, and Ferritic Steel Weld Metal Produced by Arc Welding*. IIW Doc. II-1051-85, AWS A4.3-86, 1986.

16. LEE, J. Y., LEE, J. L., and CHOO, W. Y. *Thermal Analysis of Trapped Hydrogen In AISI 4340 Steel*. in *Current Solutions to Hydrogen Problems in Steel*. Interante and Pressouyre, ed., ASM, Metals Park, OH, p. 421-427.

A 72-hour outgassing time was chosen because most of the hydrogen will outgas during that time. Also, this conformed to the requirements of the AWS A4.3-86 standard for a 45°C outgassing temperature. The A36 specimen material, milled surface finish, and other portions of the AWS A4.3-86 standard were also chosen in order to be able to compare our data with other laboratories.

Certified cylinders of specially mixed shielding gas were used throughout this study in order to ensure that the amount of hydrogen added to the welding arc atmosphere was exactly known. The GMAW process was used with DCEP and E-70S-1 electrode wire. A thermocouple was harpooned into the solidifying weld pool on representative weld samples in order to measure the thermal factor as defined by Terasaki.

## EXPERIMENTAL RESULTS

In general, it was found that conformance to AWS A4.3-86 will produce accurate and reproducible measurements of the diffusible weld hydrogen content. However, two precautionary measures must be mentioned.

The calibration procedure provided in the instruction manual of the Yanaco hydrogen analyzer can produce erroneous results. During calibration, the amount of hydrogen measured will vary with a number of factors. These include: (1) the size of the specimen chamber, (2) whether a specimen is in the chamber, (3) use of the bypass valve, and (4) the pressure of the carrier gas (including the pressure drop associated with the long length of small tubing used in the unit), each of which affect the calibrated value. Thus, a short experiment must be performed, before attempting to measure diffusible hydrogen values, in order to determine the difference between calibrating in the bypass mode and calibrating with a specimen in the chamber. Failure to determine this offset can result in up to a 25% error in the value of diffusible hydrogen measured. This is explained in more detail by Gedeon.<sup>2</sup>

The composition of the diffusible hydrogen specimen was found to affect the diffusible hydrogen value. While the variation between heats of A36 steel will not affect the measured value, drastic compositional changes were found to have a large effect.

The diffusible hydrogen determined in our laboratories as a function of hydrogen added to the argon GMA weld shielding gas is shown in Figure 4.

Using the diffusible hydrogen results obtained in our laboratories,<sup>2</sup> converting to ml/100-g fused metal and applying the conversion factor from Terasaki's analysis,<sup>3</sup> the hydrogen initially absorbed as a function of hydrogen in the weld shielding gas was found for various gas mixtures. In order to compare our results with thermodynamic data, the experimental data has also been converted to parts per million using the conversion

$$1 \text{ ml H}_2 / 100\text{-g steel} = 1.1 \text{ ppm.} \quad (3)$$

The resulting data for hydrogen initially absorbed by the weld pool as a function of diatomic hydrogen added to the pure argon GMAW shielding gas are shown in Figure 5.

If this is compared to Figure 1 and the results of other researchers, it is again found that Sievert's law will predict impossibly high hydrogen absorption temperatures. In order to explain this discrepancy, a new model of hydrogen absorption will now be presented.

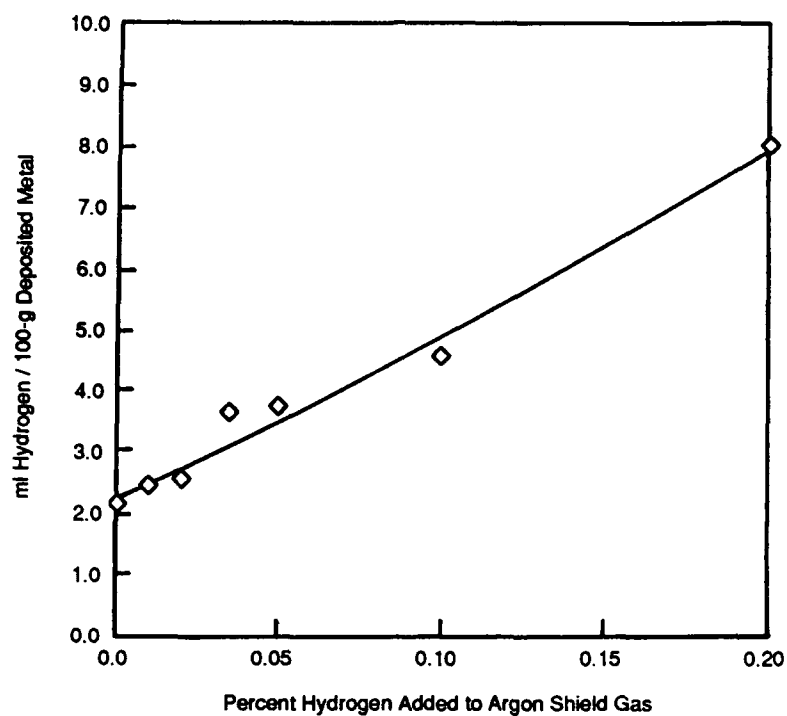


Figure 4. Diffusible hydrogen as a function of hydrogen in pure argon GMAW shielding gas.

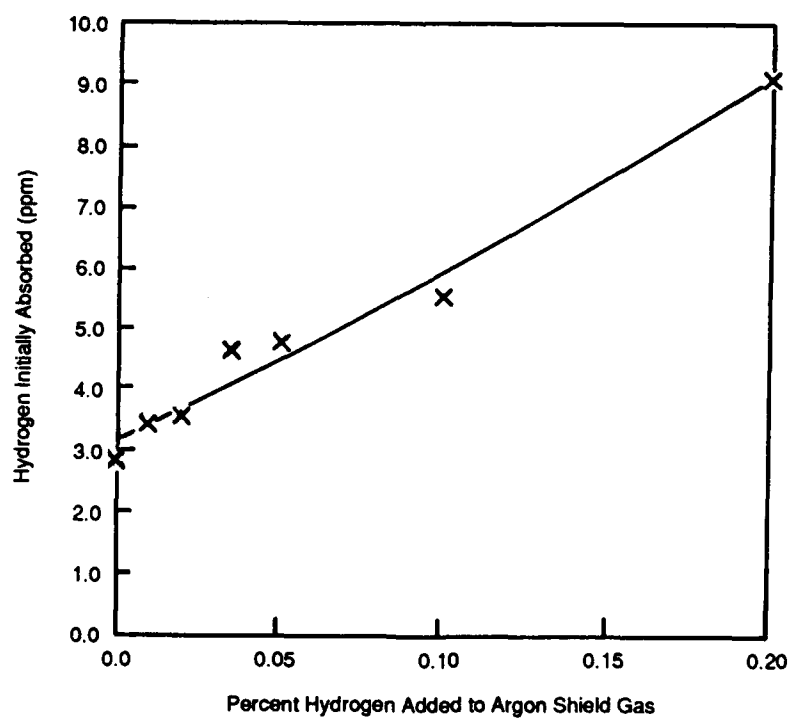


Figure 5. Initially absorbed hydrogen as a function of hydrogen in pure argon GMAW shielding gas.

## THERMODYNAMIC ANALYSIS

Sievert's law assumes that diatomic gas is absorbed into the weld pool at a single equilibrium temperature. The appropriate equations and figures governing this absorption were discussed in the Introduction. Previous research and the present experimental results show that this assumption is invalid for modelling the hydrogen absorption process.

The ensuing thermochemical analysis is based on a two-step model which postulates that hydrogen will dissociate at a reaction temperature governed by the temperature of the cathode boundary layer, and that both diatomic and monatomic hydrogen absorption will take place at a reaction temperature governed by the temperature of the weld pool surface.

### Absorption of Monatomic Hydrogen Into the Weld Pool

If one considers the following two reactions for which thermodynamic data are known,<sup>1</sup>



one can combine them into the reaction



The free energy associated with Equation 6 is equal to

$$\Delta G = -44,780 + 3.38 T \text{ (kcal / mole)}. \quad (7)$$

Thus, one can plot the amount of absorbed hydrogen as a function of the partial pressure of monatomic hydrogen for various assumed reaction temperatures as shown in Figure 6. This is replotted as absorbed hydrogen as a function of assumed reaction temperature for various partial pressures of monatomic hydrogen in Figure 7. These graphs show quite a different relation than the nondissociated hydrogen in Figures 1 and 2; namely, that the amount of absorbed hydrogen decreases with temperature rather than increases.

The fact that the solubility of "active" gases increases with decreasing temperature is known to occur in high temperature systems.<sup>17</sup> Gaseous solubility in aqueous solutions can be described as "physical" or "chemical." The solubility of diatomic hydrogen in liquid iron may be described as "physical," whereas the solubility of monatomic hydrogen in liquid iron may be described as "chemical." The partial molar heat effects for chemical solubility are usually exothermic, and the excess entropies of mixing are expected to be negative.

Since the amount of hydrogen absorbed from even a minute amount of dissociated hydrogen gas is quite large at low temperatures, the degree of dissociation must be further investigated.

17. FLENGAS, S. N., and BLOCK-BOLTEN, A. *Solubilities of Reactive Gases in Molten Salts* in *Advances in Molten Salt Chemistry*. E. J. Braunstein, G. Mamontov, and G. Smith, ed., Plenum Press, New York, 1973, p. 27-81.

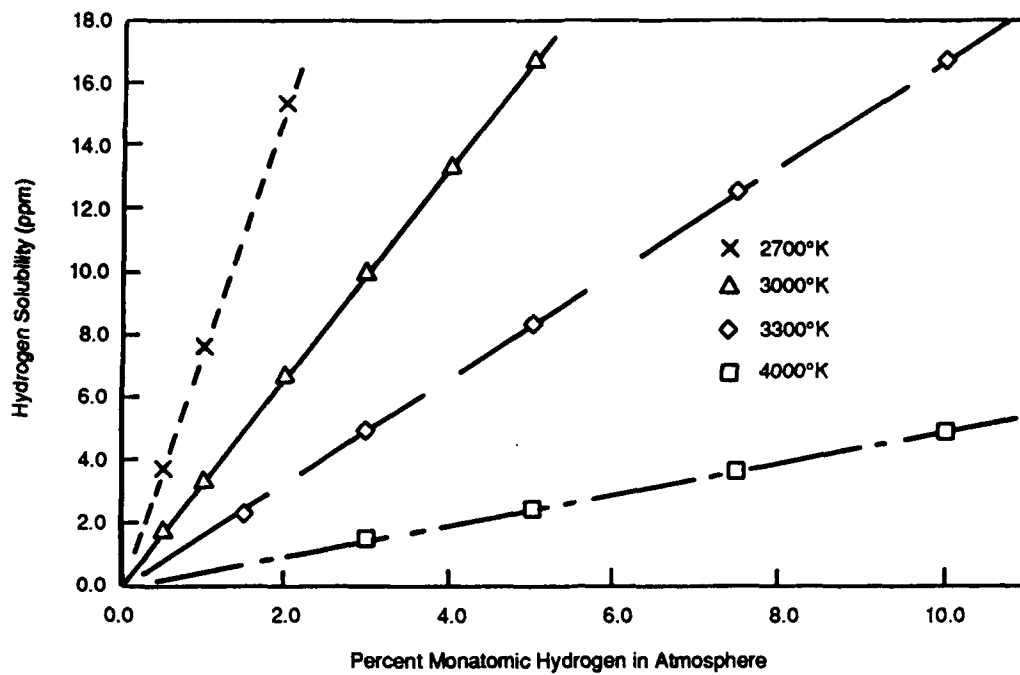


Figure 6. Equilibrium hydrogen solubility as a function of the partial pressure of monatomic hydrogen gas for various assumed absorption temperatures.

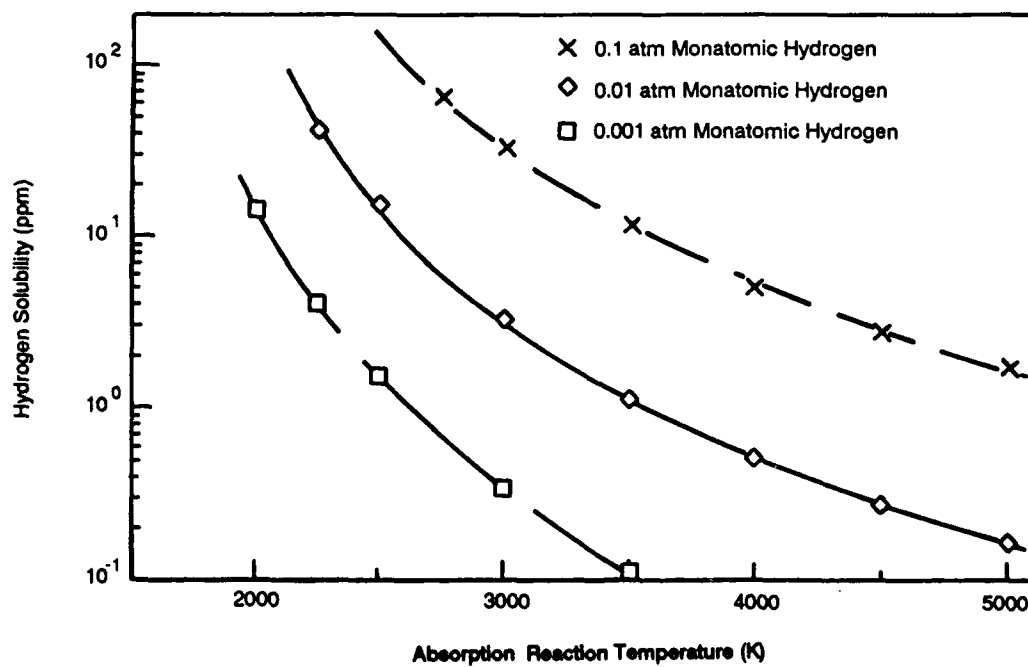


Figure 7. Equilibrium hydrogen solubility as a function of the absorption temperature for various partial pressures of monatomic hydrogen.

## Hydrogen Dissociation in the Welding Arc

The degree of hydrogen dissociation as a function of temperature and pressure has been calculated by Gedeon,<sup>2</sup> and is reproduced in Figure 8. This logarithmic family of sigmoidal curves was calculated for a total pressure (diatomic hydrogen, plus monatomic hydrogen, plus an inert shielding gas such as argon) of one atmosphere.

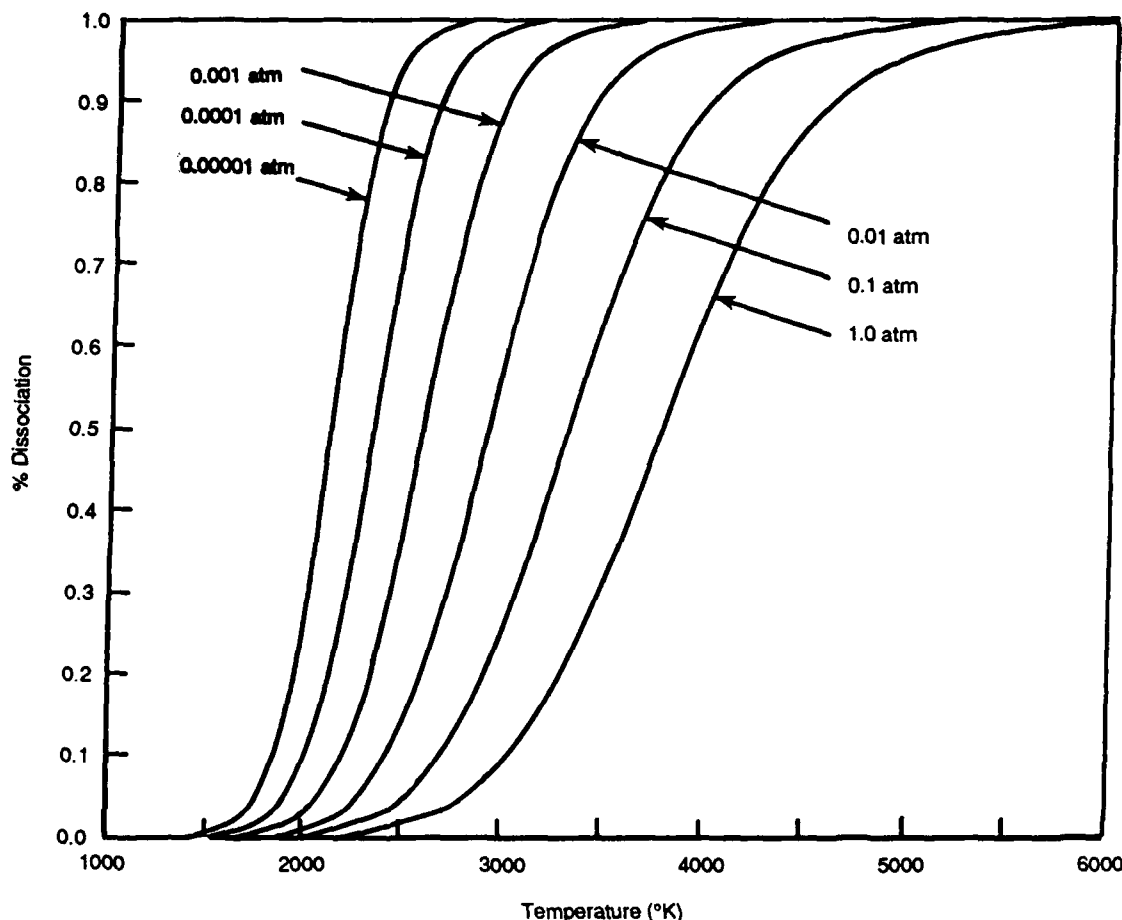


Figure 8. Fraction of hydrogen dissociated as a function of both partial pressure and temperature.

As can be seen, changes in the pressure of diatomic hydrogen can result in a large variation in the percent dissociation anticipated. At an assumed equilibrium dissociation temperature of 3000°K, the percent dissociation rises from 8% to 32% by reducing the pressure of hydrogen from 1 atmosphere to 0.05 atmospheres. It rises to virtually 100% at 0.0001 atmospheres. This is a logical extension of Le Chatelier's principle in that the diatomic molecules will seek to fill the volume available more effectively by dissociating at low partial pressures.

Thus, the amount of dissociation occurring in the high temperature region of the welding arc plasma can have a significant effect on the amount of monatomic hydrogen available for absorption. Also, at the hydrogen amounts present in welding, the bulk of the hydrogen may actually be in the form of monatomic hydrogen rather than diatomic hydrogen. As previously shown, monatomic hydrogen absorbs more readily into a weld pool than does diatomic hydrogen. Thus, the amount of hydrogen absorbed will strongly depend on the dissociation temperature.

## The Effect of Dissociation in the Cathode Boundary Layer on the Amount of Hydrogen Absorbed Into the Weld Pool

There are very large temperature gradients in the welding arc plasma. The most extreme gradients exist in the cathode and anode boundary layers where the temperature will drop from the high temperature plasma to the temperature of the weld pool over a distance of less than a millimeter. In GMAW (normally performed with reverse polarity), the weld pool will be the cathode. In GTAW (normally straight polarity), the weld pool will be the anode.

The vast majority of arc plasma physics research has been performed on the anode boundary layer, rather than the cathode boundary layer due to the added complexity of the cathode region. The temperature immediately above the cathode boundary layer must be greater than 8000°K in order to ionize the gas so that current can flow across the arc. Current flow across the cathode boundary layer is due to thermionic emission, positive ion bombardment, and field emission.

Dinulescu and Pfender,<sup>18</sup> studying anode boundary layers, found that substantial deviations from local thermal equilibrium (LTE) occurred. A detailed numerical calculation using plasma physics showed that a number of different boundary layers are involved. The thermal boundary layer is approximated by the energy exchange free path,  $\lambda_E$ , which can be interpreted as the distance traveled by an electron in the direction of the electric field over which it loses its excess energy by collisions with the heavy particles. The diffusion boundary layer is approximated by the recombination free path,  $\lambda_r$ , which can be interpreted as the distance traveled by an electron in the direction of the electric field between two successive ionization-recombination collisions.

The electrons contained in a layer adjacent to the anode of thickness  $\lambda_E$  will arrive at the anode without suffering any further energy losses by collisions with heavy particles.<sup>18</sup> By analogy, a proton (or ionized monatomic hydrogen) contained in a layer adjacent to the cathode of thickness  $\lambda_E$  will arrive at the cathode at a substantially higher temperature than the heavy species; i.e., argon. Thus, the temperature of monatomic hydrogen will probably be higher than the temperature of either the weld pool surface or the argon in the cathode region. Dinulescu and Pfender<sup>18</sup> estimate  $\lambda_E$  to be about 0.2 mm and  $\lambda_r$  to be about 0.3 mm to 0.6 mm. Quigley et al.,<sup>7</sup> also found that there would be virtually no electron collisions across the anode boundary layer (which is about 6 to 10 times thicker than the cathode boundary layer).

Based on these values, a positive hydrogen ion in the high temperature arc could travel through the cathode boundary layer and strike the weld pool without losing its thermal or kinetic energy through collision. The fact that the cathode requires positive ion bombardment in order to allow current flow further supports this hypothesis. Thus, it is reasonable to assume that the hydrogen molecules, which dissociate in the high temperature region of the arc, may not completely recombine before striking the weld pool. This deviation from LTE can be approximately modelled by assuming two different equilibrium reaction temperatures.

The justification for this dual temperature assumption is based on the fact that dissociation of diatomic hydrogen into monatomic hydrogen occurs within the cathode boundary region where temperature is ill-defined and thermodynamic equilibrium is not achieved.

18. DINULESCU, H. A. and PFENDER, E. *Analysis of the Anode Boundary Layer of High Intensity Arcs*. Journal of Applied Physics, v. 51, no. 6, p. 3149-3157.



The only definitive statement that can be made is that the temperature of the boundary layer must lie between the plasma temperature and the temperature of the weld pool. The absorption is believed to occur at the temperature of the liquid weld-pool surface.

Table 1 demonstrates the resulting hydrogen absorption if the dissociation reaction and absorption reaction occur at different temperatures. As can be seen, appropriate hydrogen absorption values can be readily calculated if the dissociation temperature is about 10% to 20% higher than the absorption temperature. By using this model, a reasonable weld pool temperature can be used for absorption, and a dissociation temperature can be determined so that the amount of hydrogen absorbed will equal experimental observations.

Table 1. HYDROGEN ABSORPTION AS A FUNCTION OF ASSUMED DISSOCIATION AND ABSORPTION REACTION TEMPERATURES

Hydrogen (%)	Dissociate Temperature (°K)	Dissociation (%)	Pressure Diatomic (atm)	Pressure Monatomic (atm)	Absorption Temperature (°K)	Hydrogen Due to Diatomic (ppm)	Hydrogen Due to Monatomic (ppm)	Total Hydrogen (ppm)
1	3000	58.0	0.00420	0.01160	2100	2.05	96.90	98.95
1	3000	58.0	0.00420	0.01160	2300	2.46	38.10	40.56
1	3000	58.0	0.00420	0.01160	2500	2.87	17.40	20.27
1	3000	58.0	0.00420	0.01160	2700	3.27	8.90	12.17
1	2700	25.3	0.00747	0.00560	2100	2.74	46.80	49.54
1	2700	25.3	0.00747	0.00560	2300	3.28	18.40	21.68
1	2700	25.3	0.00747	0.00560	2500	3.83	8.40	12.23
1	2700	25.3	0.00747	0.00560	2700	4.33	4.33	8.66
1	2500	13.5	0.00865	0.00275	2100	2.95	22.90	25.85
1	2500	13.5	0.00865	0.00275	2300	3.53	9.00	12.53
1	2300	5.5	0.00945	0.00110	1900	2.47	28.40	30.87
1	2300	5.5	0.00945	0.00110	2100	3.08	9.20	12.28
1	2500	13.5	0.00865	0.00560	2250	3.39	11.20	14.59
1	2100	1.9	0.00981	0.00038	1900	2.52	9.82	12.34

Using an estimated weld pool temperature for hydrogen absorption of 2300°C, a dissociation reaction temperature of 2500°C will result in hydrogen absorption values which are in close agreement with experimental observations. If a 2000°C weld pool temperature is assumed, then a dissociation temperature of about 2100°C will result in experimentally determined hydrogen contents.

The agreement between experimental and theoretical results now rests on the choice of weld pool temperature. The choice of weld pool temperature will dictate the resulting calculated dissociation temperature. This is important since hydrogen absorption must take place at the same temperature as the weld pool surface. However, since the weld pool temperature is far from homogeneous, the effect of temperature distribution must be considered.

#### The Effect of Radial Temperature Distribution in the Weld Pool

In the previous section, a homogeneous weld temperature and dissociation, or boundary-layer, temperature were implicitly assumed. The effect of radial temperature distribution will now be considered.

The exact temperature distribution of a GMA weld pool is not known. What is known is that the maximum temperature near the center cannot be greater than  $2600^{\circ}\text{C}$ , and that the temperature gradient at the edge of the weld pool must be negative in order for thermal conduction to be operative. Vigorous convection will make the boundary-layer thickness near the edge of the weld quite narrow so that the temperature will remain fairly constant throughout the rest of the pool. For the present, the results of Krause<sup>9</sup> for the measured temperature of a GTA weld will be used to approximate the temperature of a GMA weld.

Based on the research of Dinulescu and Pfender,<sup>18</sup> a homogeneous cathode boundary-layer thickness (and temperature) will be assumed. It is quite possible that the boundary will be thicker near the outer radius of the weld pool, and thus cooler. However, this consideration is beyond the scope of the present research.

If a dissociation temperature of  $2500^{\circ}\text{K}$  is assumed, Figure 9 shows the calculated amounts of hydrogen absorbed from both diatomic and monatomic hydrogen gas at various locations in the weld pool. An immediate observation is that the majority of the hydrogen absorption will take place around the outer edge of the weld pool. Also, it can be seen that monatomic hydrogen absorption dominates the contribution to the total hydrogen content. This is a direct contradiction to the postulates of others who have used Sievert's law to show that the maximum absorption occurred in the high temperature central region.

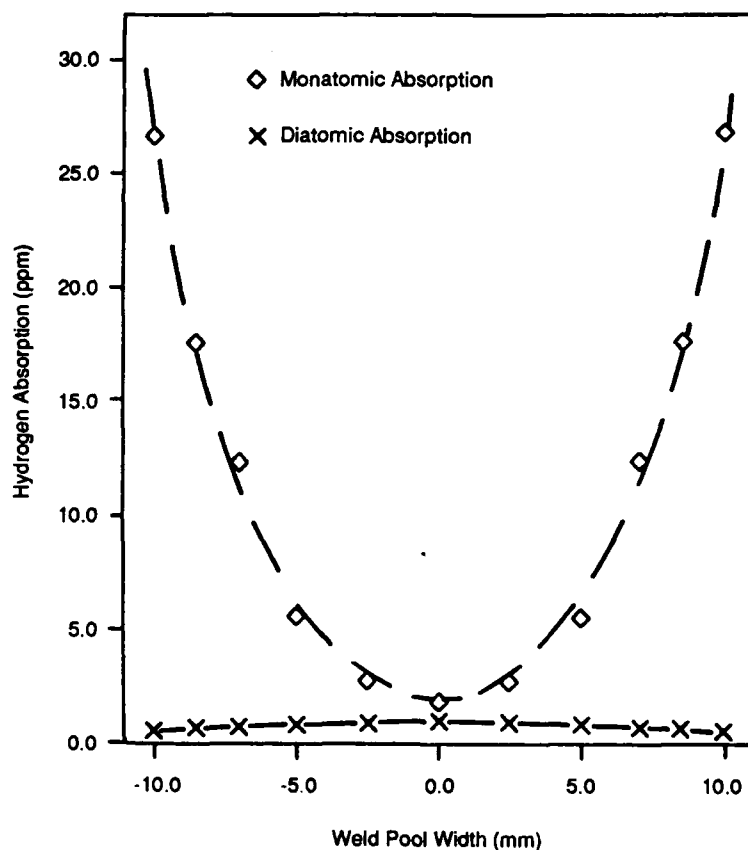


Figure 9. Theoretical hydrogen absorption due to both monatomic and diatomic hydrogen as a function of weld pool location. The calculated points assume a dissociation temperature of  $2500^{\circ}\text{C}$ , 0.01 atm hydrogen added to the argon shielding gas, and an absorption temperature as given by Krause (Ref. 9) for the surface temperature of the molten weld pool.

## DISCUSSION

### Theoretical Assumptions

The previous set of thermodynamic calculations form the core of this newly proposed model for hydrogen absorption. During these calculations, a number of assumptions had to be made in order to eliminate the need for a more detailed analysis.

The assumption of a single-reaction temperature governing the dissociation in the cathode boundary layer is probably not valid. A more valid approximation is that of a dissociation temperature distribution in the radial direction that is a percentage of the difference between the weld-pool temperature and the arc-plasma temperature. Another complicating factor is that hydrogen absorbed onto the surface of the weld pool will be affected by convection and the advancing solidification front in a moving weld pool.

Most of the hydrogen absorbed into the outer region of the weld pool will become evenly distributed throughout the pool due to vigorous convection within the pool. The hydrogen which flows to the outer regions of the pool may desorb. However, near the trailing edge of the pool, solidification may be rapid enough to trap hydrogen into the advancing solidification front. Chew and Willgoss<sup>13</sup> found that hydrogen will accumulate in the weld pool near the trailing edge, even though they postulated that hydrogen was absorbed into the center of the weld pool. Another rationale for the hypothesis that hydrogen is trapped rather than rejected by the advancing solidification front is the fact that little porosity is found in steel welds. If substantial amounts of hydrogen were being rejected, significant levels of porosity would be seen as well (such as found in aluminum welds).

Howden<sup>19</sup> also postulated that hydrogen would be "pumped" into the solidifying weld metal, rather than hydrogen being rejected at the solidification front, as had been previously thought by some. His research results agree with the present trapping hypothesis even though he assumed that the majority of the hydrogen was initially absorbed into the center of the weld pool.

If one assumes that the hydrogen which is trapped in the solidified metal is approximated by the amount initially absorbed into the trailing edge of the weld, the reaction temperature of interest will be approximately 1540°C. Using this as the absorption temperature, the calculated dissociation temperature (at the outer edge of the cathode boundary layer) which results in the experimentally observed hydrogen content, corresponds to 1900K to 2000K (about 10% greater than the absorption temperature). In fact, the hydrogen will only absorb onto the top surface of the weld stagnant layer, and there will be less hydrogen near the root of the weld. In this case, the calculated dissociation temperature will be substantially higher.

Due to the complexity of the proposed mechanism and the many assumptions and estimates involved, an exact calculation for the temperature of dissociation is not appropriate at this time. From all of the above considerations, however, it is apparent that the temperature of dissociation will be higher than the weld pool temperature at the point of absorption. This consideration allows one to model the absorption process, assuming that the hydrogen absorption temperature is equal to the experimentally measured weld pool surface temperature.

19. HOWDEN, D. G. *Behavior of Hydrogen in Arc Weld Pools*. Proc. Weld Pool Chemistry and Metallurgy International Conference, London, April 1980, p. 205-215.

The proposed model can be used to predict a number of phenomena which previous theories could not address. For example, since this theory predicts that hydrogen is primarily absorbed into the outer circumference of the weld pool, convection patterns which flow from the outer edge toward the hot center of the weld pool should have less hydrogen than welds which force the hydrogen at the edge of the pool downward to be trapped by the advancing solidification front. Also, since this theory predicts that ionized hydrogen may be present in the cathode boundary layer, there may be an electrochemical effect that will draw hydrogen toward the cathode. If all other effects are equal, this theory predicts that DCEP welds will have more hydrogen than DCEN welds.

This analysis can also be used to clarify the results of others. For example, many researchers have concluded that an increase in weld current decreases the hydrogen absorbed and, hence, the equilibrium temperature. However, a simple alternative explanation is that increasing the current will slow the cooling rate, thereby allowing more hydrogen to escape during cooling of the weld. This misunderstanding was caused by using diffusible hydrogen measurements rather than the amount of hydrogen initially absorbed.

Hopefully, a more fundamental approach to the chemical reactions occurring within the weld pool, such as taken in this work, will also be useful for understanding other gas-metal reactions occurring during welding, such as nitrogen absorption. Researchers studying nitrogen absorption in arc-melted iron<sup>14</sup> found that the arc substantially increased the nitrogen content above that predicted from the known temperature of the molten metal. Because the resulting experimental curve was parabolic, they assumed that Sievert's law still applied, even though the free energy of formation (absorption) was no longer accurate. Also, they neglected to consider the possibility that reduced partial pressures will increase the amount of dissociation at a given temperature (a piece of information not available which had to be calculated for this study). Because of this, they were unable to satisfactorily explain the resulting increase in solubility during arc melting. If a two-step absorption process including dissociation is used to model their results, then their experimental data can be satisfactorily explained.

#### **Fundamentals of Thermochemical Reaction Theories in Weld Pools**

The fact that hydrogen solubility versus diatomic hydrogen pressure in the welding arc can be approximated by a parabolic function is a spurious relationship which has, unfortunately, led many researchers to assume that Sievert's law was responsible for the shape of the curve. The functional relationship resulting from the present hypothesis between the absorbed hydrogen and hydrogen partial pressure is a very complex function. This function may resemble a square root function, but this does not mean that, in fact, it is a result of Sievert's law.

In the chemical reaction given by Equation 4, the two end conditions (hydrogen gas and hydrogen in solution) are thermodynamic state functions. State functions are conditions which can be completely specified by their extensive parameters (mole fraction, volume, and internal energy) and a combination of intensive parameters, i.e., temperature and pressure. In Sievert's law, a theoretical analysis is developed which relates the difference between the two state functions. This relationship is valid under equilibrium conditions if the system is isothermal and closed. However, in welding, this simple closed system model is not valid. Work, heat, and matter all cross the boundary in this open system. Since the arc and weld pool are not a closed system at equilibrium, it is inappropriate to apply Sievert's law to this system.

The hypothesis proposed in this study is that the energetically favored path consists of hydrogen dissociation followed by monatomic hydrogen absorption. Using this path, the estimated temperatures of the weld pool are meaningful and realistic, even though full equilibrium is not attained. When the Sievert law path of direct diatomic hydrogen absorption is assumed, the calculated weld pool temperatures are unrealistically high.

### CONCLUSION

*Concluded*  
The hydrogen content measured in a diffusible hydrogen test will be governed by three distinctly different phenomena: (1) hydrogen absorption into the molten pool, (2) hydrogen trapping or rejection from the solidification front, and (3) hydrogen diffusion away from the solidified weld. These are separate occurrences which must be separately modelled in order to obtain a complete understanding of the hydrogen remaining in the weld.

This study has separated out these various effects in order to determine the amount of hydrogen initially absorbed. Once this value is known, a new model can be developed in order to gain a greater understanding of the basic gas metal reaction occurring in the weld pool, and how it is affected by the welding arc. *Keyword: Thermoch*

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